

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)



EP 0 361 494 B1

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
07.02.1996 Bulletin 1996/06

(51) Int. Cl.<sup>6</sup>: C08F 4/654, C08F 10/00

(21) Application number: 89118026.7

(22) Date of filing: 29.09.1989

### (54) Components and catalysts for the polymerization of olefins

Bestandteil und Katalysator für Olefinpolymerisation

Composants et catalyseurs pour la polymérisation d'oléfines

(84) Designated Contracting States:  
AT BE DE ES FR GB IT NL SE

- Noristl, Luciano  
I-44100 Ferrara (IT)
- Scordamaglia, Raimondo  
I-20154 Milano (IT)
- Barino, Luisa  
I-28100 Novara (IT)
- Giannini, Umberto  
I-20133 Milano (IT)
- Morini, Giampiero  
I-27058 Voghera Pavia (IT)

(30) Priority: 30.09.1988 IT 2215088

(43) Date of publication of application:  
04.04.1990 Bulletin 1990/14

(73) Proprietor: MONTELL NORTH AMERICA INC.  
New Castle County Delaware (US)

(72) Inventors:

- Albizzati, Enrico  
I-28041 Arona Novara (IT)
- Barbe', Pier Camillo  
I-44100 Ferrara (IT)

(74) Representative: Zumstein, Fritz, Dr. et al  
D-80331 München (DE)

(56) References cited:  
EP-A- 0 086 473  
US-A- 4 469 648

GB-A- 966 025

## Description

The present invention relates to solid components of catalysts for the polymerization of olefins and the catalysts obtained therefrom. The catalysts including titanium compounds supported on magnesium halides in active form are well known in the art.

Catalysts of this type are described for the first time in the USA patent No. 4,298,718. Said catalysts are formed on titanium tetrahalides supported on halides of magnesium in active form.

Although the catalysts have high activity in the polymerization of ethylene as well as alpha olefins like propylene and butene-1, they are not very stereospecific.

Improvements to stereospecificity have been made by adding electron-donor compounds to the solid catalyst component (U.S. patent No. 4,544,717).

Substantial improvements were made using, in addition to the electron-donor present in the solid component, an electron-donor added to the Al-alkyl co-catalyst component (U.S. patent No. 4,107,414).

The catalysts modified in this manner although they are highly stereospecific (isotactic index about 94-95) still do not show sufficiently high levels of activity.

Significant improvements in activity and stereospecificity were obtained by preparing the solid catalytic component according to the technique described in U.S. patent No. 4,226,741.

High level performance in catalyst activity as well as stereospecificity have been obtained with the catalysts described in European patent No. 045977. Said catalysts have as a solid catalyst component, a magnesium halide in active form on which is supported a titanium halide preferably  $TiCl_4$  and an electron-donor compound selected from specific classes of carboxylic acid esters, of which the phthalates are typical examples, and, as a co-catalyst component, a system formed of an Al-triethyl compound and a silicon compound containing at least one Si-OR bond (R hydrocarbyl radical). After the appearance of the above mentioned patents which mark the fundamental step for the development of the coordination catalysts supported on magnesium halides, many patents have been filed with the purpose of modifying and/or improving the performance of the above mentioned catalysts.

In the prolific patent and scientific literature available, however, there is no description of catalysts endowed with both high activity and stereospecificity in which the electron-donor of the solid catalyst component is the only donor present in the catalyst system. The catalysts known up to now that have both high activity and stereospecificity always include the use of an electron-donor in the solid catalyst component and in the co-catalyst component.

Surprisingly, it has now been found that it is possible to prepare highly active and stereospecific catalysts where the only donor used is present in the solid catalyst component.

An object of the present invention is a solid catalyst component for the polymerization of olefins having the features defined in claim 1; specific embodiments are defined in the claims dependent on claim 1.

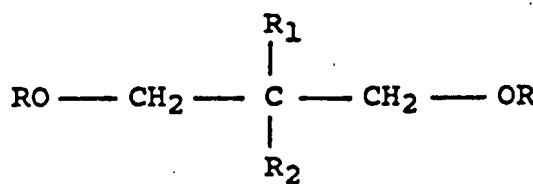
The donors used in the catalyst components of this invention are ethers which satisfy particular requisites of reactivity towards anhydrous magnesium dichloride and titanium tetrachloride.

The ethers of the invention form complexes with anhydrous magnesium dichloride but in a quantity of less than 60 mmoles per 100 g of  $MgCl_2$ ; with  $TiCl_4$  the ethers do not undergo at all substitution reactions or they react this way for less than 50 % in moles.

Preferably the ethers form complexes with anhydrous magnesium dichloride in quantities comprised between 20 and 50 mmoles, and react with  $TiCl_4$  for less than 30%.

The procedures for the tests of activated anhydrous magnesium dichloride complexing and reaction with  $TiCl_4$  are reported below.

Examples of suitable ethers which satisfy the reactivity criterion set forth above are 1,3-diethers of formula:



where  $R$ ,  $R_1$  and  $R_2$  independently are linear or branched alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, and  $R_1$  or  $R_2$  may also be hydrogen.

In particular  $R$  is an alkyl radical with 1-6 carbon atoms, and more specifically it is methyl. In this case, when  $R_1$  is methyl, ethyl, propyl or isopropyl,  $R_2$  may be ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, 2-ethylhexyl, cyclohexyl, methyl cyclohexyl, phenyl, or benzyl; when  $R_1$  is hydrogen  $R_2$  can be ethyl, butyl, sec.butyl, t-butyl, 2-ethylhexyl, cyclohex-

ylethyl, diphenylmethyl, p-chloropenyl, 1-naphthyl, 1-decahydronaphthyl; R<sub>1</sub> and R<sub>2</sub> can be the same and be ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, neopentyl, isopentyl, phenyl, benzyl, cyclopentyl or cyclohexyl.

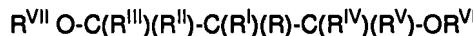
Examples of representative ethers that are included in the above formula are: 2-(2-ethylhexyl) 1,3-dimethoxypropane, 2-isopropyl- 1,3-dimethoxypropane, 2-butyl-1,3-dimethoxypropane, 2-sec-butyl-1,3-dimethoxypropane, 2-cyclohexyl-1,3-dimethoxypropane, 2-phebyl-1,3-diethoxypropane, 2-cumyl-1,3-diethoxypropane, 2-(2-pnehyilethyl)-1,3-dimethoxypropane, 2-(2-cyclohexylethyl)1,3-dimethoxypropane, 2-(p-chlorophenyl)1,3-dimethoxypropane, 2-(diphenylmethyl)-1,3-dimethoxypropane, 2-(1-naphthyl)1,3-dimethoxy propane, 2,2-fluorophenyl)-1,3-dimethoxypropane, 2-(1-decahydronaphthyl)-1,3-dimethoxypropane, 2-(p-t-butylphenyl)-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2,2-dibutyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-benzyl-1,3-dimethoxypropane, 2-methyl-2-ethyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-phenyl-1,3-dimethoxypropane, 2-methyl-2-cyclohexyl-1,3-dimethoxypropane, 2,2-bis(p-chlorophenyl)-1,3-dimethoxypropane, 2,2-bis(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-methyl-2-isobutyl-1,3-dimethoxypropane, 2-methyl-2-(2-ethylhexyl)-1,3-dimethoxy propane, 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-diethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2-isobutyl-2-isopropyl-1,3-dimethoxypropane, 2,2-di-sec-butyl-1,3-dimethoxypropane, 2,2-di-tertbutyl-1,3-dimethoxypropane, 2,2-di-neopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane, 2-phenyl-2-ebnzy1-1,3-dimethoxypropane, 2-cyclohexyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicylopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane.

Other suitable ethers are: 2,3-diphenyl-1,4-diethoxybutane, 2,3-dicyclohexyl-1,4-diethoxybutane, 2,2-dibenzyl-1,4-diethoxybutane, 2,3-dibenzyl-1,4-diemethoxybutane, 2,3-dicyclohexyl-1,4-dimethoxybutane, 2,3-diisopropyl-1,4-diethoxybutane, 2,2-bis(p-methylphenyl)1,4-dimethoxybutane, 2,3-bis(p-chlorophenyl)1,4-dimethoxybutane, 2,3-bis(p-fluorophenyl)1,4-dimethoxybutane, 2,4-diphenyl-1,5-dimethoxypentane, 2,3-diphenyl-1,5-dimethoxypentane, 2,4-diisopropyl-1,5-dimethoxypentano, 3-methoxymethyltetrahydrofuran, 3-methoxymethyldioxane, 1,1-dimethoxymethyl-decahydronaphthalene, 1,1-dimethoxymethylindane, 2,2-dimethoxymethylindane, 1,1-dimethoxymethyl-2-isopropyl-5-methylcyclohexane, 1,3-diisoamylloxypropane, 1,2-diisobutoxypropane, 1,2-diisobutoxyethane, 1,3-diisoamylloxypropane, 1,2-diisoamuloxethane, 1,3-dineopentoxypropane, 2,2-tetramethylene-1,3-dimethoxypropane, 1,2-dineopentoxethane, 2,2-tetramethylene-1,3-dimethoxypropane, 2,2-pentamethylene-1,3-dimethoxypropane, 2,2-pentamethylene-1,3-dimethoxypropane, 2,2-hexamethylene-1,3-dimethoxypropane, 1,2-bis(methoxymethyl)cyclohexane, 2,8-dioxaspiro[5,5]undecane, 3,7-dioxabicyclo[3,3,1]nonane, 3,7-dioxabicyclo[3,3,0]octane, 3,3-diisobutyl-1,5-dioxononane, 6,6-diisobutylidioxyepane, 1,1-dimethoxymethylcyclopropane, 1,1-bis[dimethoxymethyl] cyclohexane, 1,1-bis[methoxymethyl]bicyclo[2,2,1]heptane, 1,1-dimethoxymethyl cyclopentane, 2-methyl-2-methoxymethyl-1,3-dimethoxypropane.

The ethers preferred are the 1,3-diethers belonging to the general formula indicated above and in particular those where R is methyl and R<sub>1</sub> and R<sub>2</sub>, independently, are isopropyl, isobutyl, t-butyl, cyclohexyl, isopentyl, cyclohexylethyl. Ethers particularly preferred are 2,2-diisobutyl-1,3-dimethoxypropane; 2-isopropyl 2-isopentyl-1,3-dimethoxypropane; 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicylopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-isobutyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane.

The above ethers can be prepared according to the methods disclosed in published European patent application EP-A-0361493, of the same Applicant and filed on the same date as the present application with the title "Diethers Usable In The Preparation of Ziegler-Natta Catalysts".

Said EP-A-0 361 493 discloses diethers of general formula



where R to R<sup>V</sup>, same or different, are H or hydrocarbon radicals, provided that R and R<sup>I</sup> are not both H or methyl or are not methyl and propyl, and R<sup>VI</sup> and R<sup>VII</sup> are the same or different and are hydrocarbon radicals; two or more of R to R<sup>VII</sup> may be bonded to form a cyclic structure. Said diethers, used in the preparation of Ziegler-Natta catalysts, are prepared by reaction of diols corresponding to the above diethers with alkylant agent. A way of synthesis of said diols consists in the reduction of the corresponding oxidized compounds such as diketones, ketoaldehydes, dicarboxylic acids.

The ether complexing test with MgCl<sub>2</sub> is conducted as follows.

In a 100 ml glass flush with fixed blades glass mechanical agitator are introduced in a nitrogen atmosphere, in order:

- 70 ml anhydrous n-heptane

- 12 mmoles anhydrous  $MgCl_2$  activated as described below
- 2 mmoles ether.

5 The ingredients are heated at 60°C for 4 hours (stirring speed 400 rpm), then filtered and washed at room temperature with 100 ml n-heptane and dried with mechanical pump.

The quantity of ether complexed is determined, after treatment of the solid with 100 ml of ethanol, by quantitative gaschromatographic analysis.

The data relative to the complexing test are shown in Table 1.

The test for reactivity with  $TaCl_4$  is conducted as follows.

10 In a 25 ml test tube with a magnetic agitator are introduced, in a nitrogen atmosphere, in order:

- 10 ml anhydrous n-heptane
- 5 mmoles  $TiCl_4$
- 1 mmole ether donor

15 The ingredients are heated at 70° for 30 min then cooled at 25°C and decomposed with 90 ml of ethanol.

The solution obtained is analyzed gas chromatographically with a Carlo Erba HRGC 5300 Mega Series gas chromatograph with a 25 meters Chrompack CP-SIL 5 CB capillary column. The data relative to the reactivity tests are shown in Table 1.

20 The magnesium dichloride used in the complexing test with the ethers is prepared as follows.

In a 1 l container of a vibrating mill (Siebtechnik Vibratrom) containing 1.8 kg of steel spheres 16 mm in diameter, are introduced under a nitrogen atmosphere, 50 g anhydrous  $MgCl_2$  and 6.8 ml 1,2 dichloroethane (DCE).

The mixture is milled at room temperature for 96 hours, after which the solid obtained is dried at 50°C for 16 hours under vacuum of a mechanical pump.

25 Solid characterization.

In the X-ray powder spectrum:

30

- half peak breadth of D110 reflection = 1.15 cm;
- presence of a halo with maximum intensity at angle  $2\theta = 32.1^\circ$ ;
- Surface area (B.E.T.) = 125  $m^2/g$ ;
- Residual DCE = 2.5% by weight.

35

40

45

50

55

Table 1

	Ether	Complexing with MgCl <sub>2</sub> (*)	Reaction with TiCl <sub>4</sub> (**)
5			
10	2,2-dimethyl-		
15	1,3-dimethoxypropane	3,5	80
20	2-methyl-2-isopropyl-		
25	1,3-dimethoxypropane	1,6	71
30	2,2-diisobutyl-		
35	1,3-dimethoxypropane	3,3	98
40	2,2-diisobutyl-		
45	1,3-diethoxypropane	2,0	100
50	2,2-diisobutyl-		
55	1,3-di-n-butoxypropane	0,5	97
60	2,2-diphenyl-		
65	1,3-dimethoxypropane	0,7	75
70	2,2-bis (cyclohexylmethyl)-		
75	1,3-dimethoxypropane	1,8	85
80	1,3-diisobutoxypropane	2,6	99

Table 1 (follow)

5

2,2-pentamethylene-

10	1,3-dimethoxypropane	2,4	100
<hr/>			
15	1,1-bis(methoxymethyl)		
<hr/>			
20	bicyclo-(2,2,1-heptane)	1,9	93
<hr/>			
25	1,3 dimethoxypropane	9,6	100
<hr/>			
30	1-isopropyl-2,2-dimethyl-		
<hr/>			
35	1,3-dimethoxypropane	1,3	0
<hr/>			
40	2-isopentyl-2-isopropyl-		
<hr/>			
45	1,3-dimethoxypropane	2,5	98
<hr/>			
50	1,2 dimethoxyethane	9,4	76
<hr/>			

(\*) Moles of ether X 100      complexed by 100 g of MgCl<sub>2</sub>(\*\*) Percentage in moles of ether recovered after reaction with  
TiCl<sub>4</sub>

45      The preparation of the solid catalyst component including the ethers of the invention is carried out according to various methods.

For example, the magnesium dihalide (used in anhydrous state containing less than 1% of water), the titanium compound and the di or polyether are ground together under conditions where activation of the magnesium dihalide occurs. The milled product is then treated one or more times with TiCl<sub>4</sub> in excess at temperatures between 80 and 135°C and then washed repeatedly with a hydrocarbon i.e. hexane until all chlorine ions disappear.50      According to another method, the anhydrous magnesium dihalide is preactivated according to known methods in the prior art and then reacted with an excess of TiCl<sub>4</sub> which contains the ether compound in solution, at temperatures between 80 and 135°C. The treatment with TiCl<sub>4</sub> is repeated and the solid is then washed with hexane to eliminate all traces of unreacted TiCl<sub>4</sub>.55      According to another method, an MgCl<sub>2</sub> nROH adduct (particularly in form of spheroidal particles) in which n is a number from 1 to 3, and ROH is ethanol, butanol, or isobutanol, is treated with an excess of TiCl<sub>4</sub> containing the ether compound in solution at a temperature generally between 80 and 120°C. After the reaction, the solid is treated once more with TiCl<sub>4</sub>, then separated and washed with a hydrocarbon until the chlorine ions are removed.

According to another method, carboxylates or halocarboxylates of magnesium or alcoholates or chloroalcoholates of magnesium, the chloroalcoholates prepared according to U.S. patent No. 4,220,554 are treated with  $TiCl_4$  in excess containing the ether compound in solution, under reaction conditions described above.

According to another method complexes of magnesium halide with titanium alcoholates for example the complex  $MgCl_2 \cdot 2Ti(OC_4H_9)_4$  are treated, in a hydrocarbon solution, with  $TiCl_4$  in excess containing the ether compound in solution. The solid product is separated and further treated with an excess of  $TiCl_4$  and then separated and washed with hexane. The reaction with  $TiCl_4$  is conducted at temperatures between 80 and 120°C.

According to a variant of the above method, the complex between  $MgCl_2$  and the titanium alcoholate is reacted in hydrocarbon solution with hydropolyxyloxane. The separated solid product is reacted at 50°C with silicon tetrachloride containing the ether compound in solution and the solid is treated with  $TiCl_4$  in excess operating at 80-100°C. It is possible to react with  $TiCl_4$ , in excess, containing the ether compound in solution, porous styrene-divinylbenzene resins in spherical particle form, impregnated with solutions of compounds or complexes of Mg soluble in organic solvents.

The resins and their method of impregnation are described in EP-A-344 755.

The reaction with  $TiCl_4$  is carried out at 80-100°C and after separating the  $TiCl_4$  excess, the reaction is repeated and the solid is then washed with a hydrocarbon.

The molar ratio  $MgCl_2$ /ether compound used in the reactions indicated above is generally between 4:1 and 12:1.

The ether compound is present in the magnesium halide containing component in quantities generally between 5 and 20% mole with respect to the magnesium dihalide.

However, in the case of components supported on resins, the molar ratio between fixed ether compound and the magnesium present in generally between 0.3 and 0.8.

In the catalyst components of the invention the ratio Mg/Ti is generally between 30:1 and 4:1; in the components supported on resins the ratio is lower, generally from 2:1 to 3:1.

The titanium compounds that can be used for the preparation of catalytic components are the halides and halogen alcoholates. Titanium tetrachloride is the preferred compound. Satisfactory results are obtained also with trihalides, particularly  $TiCl_3$  HR,  $TiCl_3$  ARA, and with haloalcoholates, such as  $TiCl_3OR$ , where R is a phenyl radical.

The above mentioned reactions result in the formation of magnesium dihalide in active form.

In addition to these reactions, other reactions that result in the formation of magnesium dihalide in active form starting with magnesium compounds different from halides are well known in literature.

The active magnesium dihalides present in the solid catalyst components of the invention show in the X-ray powder spectrum of the catalyst component the replacement of the most intense diffraction present in the powder spectrum of the non-activated magnesium halides having a surface area of less than  $3 m^2/g$  by a halo with the maximum intensity peak shifted with respect to the position of the most intense diffraction line, or a half peak breadth of the most intense diffraction line at least 30% greater than the half peak breadth of the corresponding line of the non-activated magnesium halide. The most active forms are those where in the X-ray powder spectrum of the catalyst component a halo appears.

Among the magnesium dihalides, the magnesium dichloride is the preferred compound. In the case of the most active forms of magnesium dichloride the halo appears in place of the diffraction line that is present in the spectrum of the non-active magnesium chloride at an interplanar distance of 2.56 Å.

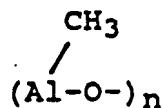
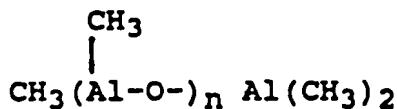
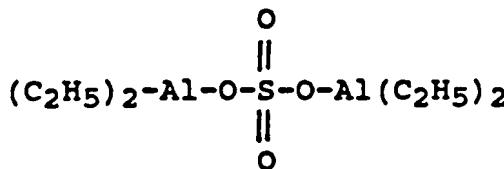
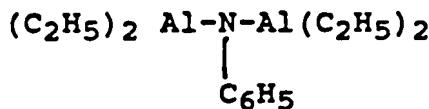
The solid catalyst component of the invention forms, by reaction with Al-alkyl compounds, catalysts for the polymerization of olefins  $CH_2=CHR$ , where R is hydrogen, alkyl radical with 1-6C, or aryl radical, or mixtures of said olefins mixed with each other with or without diolefins.

Therefore another object of the present invention is a catalyst for the polymerization of olefins having the features defined in independent claim 14; specific embodiments of said catalysts are defined in the claims depending on claim 14.

The Al-alkyl compounds include Al-trialkyl such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl. Linear or cyclic Al-alkyl compounds containing two or more Al atoms linked to each other by O, N or S atoms may be used.

Examples of these compounds are:





25 where n is a number between 1 and 20.

Also one can use AlR<sub>2</sub>OR' compounds, where R' is an aryl radical substituted in position 2 and/or 6 and R is an alkyl radical with 1-6 carbon atoms, or AlR<sub>2</sub>H compounds.

The Al-alkyl compound is used in Al/Ti ratios generally between 1 and 1000.

The trialkyl compounds may be used in mixtures with Al-alkyl halides, such as AlEt<sub>2</sub>Cl.

30 The polymerization of olefins is carried out according to known methods in a liquid phase of the monomer(s) or a solution of monomer(s) in an aliphatic or aromatic hydrocarbon solvent, or in gas phase, or with techniques using a combination of liquid phase and gas phase.

The (co)polymerization temperature is generally between 0° and 150°C, preferably between 60° and 100°C, while operating at atmospheric pressure or at a higher pressure.

35 The catalysts may be precontacted with small quantities of olefins (prepolymerization). The prepolymerization improves the catalyst performance as well as the polymer morphology.

The prepolymerization is carried out by maintaining the catalyst in suspension in a hydrocarbon solvent (hexane, heptane, etc.) while contacting small amounts of the monomer with the catalyst and polymerizing at a temperature between room temperature and 60°C producing quantities of polymer included between 0.5 and 3 times the weight of 40 the catalyst component. It may also be carried out in liquid or gaseous monomer, under the temperature conditions above, to produce quantities of polymer up to 1000 g per g of the catalyst component.

In case of stereoregular polymerization of olefins, in particular of propylene, sometimes it is convenient to use together with the Al-alkyl compound an electron-donor selected from 2,2,6,6,-tetramethylpiperidine and silicon compounds containing at least one Si-OR bond wherein R is a hydrocarbyl radical.

45 Preferably the silicon compounds have the formula



where R<sup>I</sup> and R<sup>II</sup> independently, are branched alkyl, cycloaliphatic or aryls radicals with 1-12 carbon atoms; R<sup>III</sup> and R<sup>IV</sup> independently are alkyl radicals with 1-6 carbon atoms.

50 Examples of such compounds are:

(t-butyl)<sub>2</sub> Si(OC<sub>3</sub>)<sub>2</sub>; (cyclohexyl)<sub>2</sub> Si(OCH<sub>3</sub>)<sub>2</sub>;  
(isopropyl)<sub>2</sub> Si(OCH<sub>3</sub>)<sub>2</sub>; (sec-butyl)<sub>2</sub> Si(OCH<sub>3</sub>)<sub>2</sub>.

The molar ratio between Al-alkyl compound and electron-donor is usually between 5:1 and 100:1.

55 As indicated above, the catalysts find particular application in the polymerization of CH<sub>2</sub>=CHR olefins where R is an alkyl radical with 1-6 carbon atoms or an aryl radical.

They are also particularly suited for the polymerization of ethylene and its mixtures with smaller proportions of alpha-olefins, such as butene-1, hexene-1 and octene-1 to form LLDPE, because the catalysts produce polymers with narrow molecular weight distribution.

In the copolymerization of ethylene with propylene, or other alpha-olefins or mixtures thereof to form elastomeric products copolymers are obtained having low crystallinity suitable therefore for the production of elastomers with highly valued qualities.

The following examples illustrate the invention.

5 In the examples, unless otherwise indicated, the percentages are by weight.  
 The solubility in xylene is determined by thermo solubilizing the polymer (130°C), cooling and then filtering it.  
 The solubility is determined by the fraction soluble at 25°C. The insoluble residue substantially corresponds to the isotacticity index determined by extraction with boiling n-heptane (4 hours). Melt index E and F for polyethylene and L for polypropylene are determined according to ASTM D1238. Melt index E and F are measured at 190°C with respective 10 weights of 2.15 and 21.6 Kg. The one for polypropylene is measured at 230°C with a weight of 2.16 Kg.  
 The intrinsic viscosity is determined in tetralin at 135°C. Unless otherwise indicated, the isotacticity index (I.I.) has been determined by extraction with boiling n-heptane (4 hours).

### Polymerization Procedure

15 A In liquid monomer  
 Procedure A.1.  
 20 In a 4 l stainless steel autoclave equipped with an anchor agitator and previously purged with nitrogen flux at 70°C for 1 hour, were introduced, under propylene flow at 30°C, 80 ml anhydrous n-hexane containing an adequate quantity of solid catalyst component and 6.9 mmoles of Al(Et)<sub>3</sub>. The autoclave was closed and 120 ml of hydrogen was introduced. The agitator was inserted and 1.2 Kg of liquid propylene, or other alpha-olefin monomer capable of being polymerized in liquid phase, was charged. The temperature was brought to 70°C in 5 minutes and the polymerization was carried 25 out for 2 hours. At the end of the test the unreacted propylene is removed, the polymer recovered and dried in an oven at 70°C under nitrogen flow for 3 hours, and then characterized.

#### Procedure A.1.1.

30 The procedure of A.1 above were followed except that added to the hexane was an appropriate quantity of an electron-donor together with Al(Et)<sub>3</sub> corresponding to a molar ratio Al/donor = 20. The composition of the solid catalyst components and the ethers used, the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3.

In table 3 the donor used together with Al(Et)<sub>3</sub> is indicated in parenthesis.

35 B In solvent.  
 Procedure B.2.  
 40 A 2.5 l stainless steel autoclave, equipped with a thermostat and magnetic agitator, which was previously purged with nitrogen flux at 70°C for 1 hour and washed 4 times successively with propylene, was heated to 45°C and, under a light nitrogen flow, 870 ml of anhydrous hexane was charged. The catalyst suspension (catalyst component and Al-alkyl premixed immediately before the test in 130 ml solvent) was then added. The autoclave was closed and 120 ml of 45 hydrogen was fed from a calibrated cylinder. The agitator was inserted and the temperature was rapidly brought to 75°C (in about 5 minutes). Gaseous propylene or other alpha-olefin monomer was then introduced up to a total pressure of 8 atm.

This condition was maintained for 4 hours continuously feeding propylene or other monomers to reintegrate the monomer polymerized. At the end of the polymerization the autoclave was rapidly degassed and cooled to 25-30°C. The polymer suspension was then filtered, the solid part was dried in an oven at 70°C in nitrogen for 4 hours and then 50 weighed and analyzed. The filtrate was evaporated and the dry residue consisting of amorphous polymer was recovered and weighed. This was taken into consideration in calculating the total yield and the total isotactic index.

#### Procedure B.2.1

55 In a 2000 ml stainless steel autoclave, equipped with an anchor agitator, was introduced under a propylene flow at 25°C 1000 ml n-heptane, 2.5 mmoles of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and an adequate quantity of the solid catalyst component. The autoclave was closed and the pressure brought to 1 atm. while feeding propylene, and an overpressure of hydrogen equal to 0.2 atm was introduced. The reaction mixture was heated to 70°C and the pressure brought to a total

of 7 atm, by feeding propylene, and polymerized for 2 hours while continuing to feed the monomer to maintain the pressure at 7 atm.

The polymer obtained was isolated by filtration and dried; the polymer remaining in the filtrate was precipitated in methanol, vacuum dried and considered in determining the total insoluble residue of the extraction with n-heptane. The composition of the solid catalyst components and ethers used and the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3.

#### Procedure B.2.2.

The polymerization methods described in procedure B.2.1. were followed except using 5 mmoles of  $Al(C_2H_5)_3$  together with an adequate quantity of electron donor such that the molar ratio  $Al/donor=20$ . The composition of the solid catalyst components, ether and electron donor (with the  $Al$ -alkyl compound) used and the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3. In table 3 the donor used together with  $Al(C_2H_5)_3$  is indicated in parenthesis.

#### Example 1

In a 1 l flask equipped with condenser, mechanical agitator and thermometer was introduced 625 ml  $TiCl_4$  under nitrogen environment. 25 g of spherical  $MgCl_2 \cdot 2.1C_2H_5OH$  support, obtained according to the procedures and ingredients of example 1 of U.S. patent 4 469 648, was fed at 0°C with agitation and heated to 100°C over 1 hour. When the temperature reached 40°C, 4.1 ml of 2,2-diisobutyl-1,3-dimethoxypropane was introduced, and the contents maintained at 100°C for 2 hours, left to settle and the supernatant siphoned off. 550 ml of  $TiCl_4$  was added to the solid and heated at 120°C for 1 hour with agitation. The agitation was stopped, the solid was allowed to settle and the supernatant was removed by siphon. The residual solid was then washed 6 times with 200 ml portions of anhydrous hexane at 60°C and 3 times at room temperature and dried under vacuum.

The catalyst solid component contained 3.45% Ti and 12.6% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure A.1 above for the liquid monomer using 0.76 g of  $Al(C_2H_5)_3$ , 0.09 ml of hexane suspension containing 7.25 mg of solid catalyst component and 1000 ml hydrogen. 460 g of polymer was obtained. The polymer yield was 63.4 Kg/g of catalyst component. The polymer has a 95.3% insoluble residue in xylene at 25°C, a melt index of 10.0 g/10' and a tamped bulk density of 0.48 g/ml.

#### Example 2

In a 500 ml glass flask equipped with condenser, mechanical agitator and thermometer, was introduced, in an anhydrous nitrogen environment at 20°C, 285 ml of  $TiCl_4$  and 20 g of  $C_2H_5OMgCl$  support prepared according to the procedure of U.S. patent n. 4,220,554. While agitating the contents were heated to 70°C in 30 minutes and then 4.7 ml 2,2-diisobutyl-1,3-dimethoxypropane was added and heated to 120°C in 30 minutes. The temperature was maintained at 120°C for 1 hour. The reaction mixture was allowed to settle and supernatant removed by siphon. Then another 285 ml  $TiCl_4$  were added and heated at 120°C for 1 hour. The reaction mixture was allowed to settle and the supernatant removed by siphon. The residual solids were washed 5 times with 150 ml portions of anhydrous heptane at 80°C, and again at room temperature with 150 ml portions of anhydrous hexane until there were no chlorine ions in the wash liquid.

The analysis of the vacuum dried solid catalyst component showed a content of 2.2% Ti and 12.2% 2,2-diisobutyl-1,3-dimethoxypropane.

Propylene was polymerized according to the Procedure A.1 above using 0.76 g  $Al(C_2H_5)_3$ , 0.12 ml hexane suspension containing 13 mg of solid catalyst component and 1000 ml hydrogen.

240 g of polymer was obtained with a polymer yield of 18.4 Kg/g catalyst component, a 95.2% insoluble residue in xylene, at 25°C, a melt index of 10.6 g/10' and a tamped bulk density of 0.50 g/ml.

#### Example 3

In a 350 ml porcelain jar containing 4 porcelain spheres, was introduced, under an anhydrous nitrogen environment, 9.2 g of commercial anhydrous  $MgCl_2$  and 3.3 ml of 2,2-diisobutyl-1,3-dimethoxypropane. The jar is placed in a centrifugal mill operated at 350 rpm for 15 hours.

In a 250 ml glass flask fitted with a condenser, mechanical agitator and thermometer, under an anhydrous nitrogen environment at room temperature, were introduced 8 g of the above milled product and 115 ml of  $TiCl_4$ .

The contents were heated to 120°C in 20 minutes and maintained at 120°C for 2 hours.

The solids were allowed to settle and supernatant was siphoned off. Another 115 ml of  $TiCl_4$  was introduced, heated at 120°C for 2 hours. The solids were allowed to settle and the supernatant removed by siphon. The solid residue was washed repeatedly at 60°C and at 40°C with 100 ml portions of anhydrous hexane, until there were no chlorine ions in

the wash liquid. The solid residue, obtained by vacuum drying, contained 2.15% Ti and 10.2% 2,2-diisobutyl-1,3-dimethoxypropane. The polymerization was carried out according to procedure B.2, using 0.57 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  and 0.25 ml hexane suspension containing 15.0 mg of solid catalyst component. 284 g of polymer was obtained with a polymer yield of 18.9 Kg/g catalyst, a 96.1% residue insoluble in xylene at 25°C, a melt index of 4.2 g/10' and a tamped bulk density of 0.35 g/ml.

5

#### Example 4

In a 350 ml porcelain jar containing 4 porcelain spheres was introduced, under an anhydrous nitrogen environment, 7.65 g of anhydrous  $\text{MgCl}_2$ , 2.76 ml 2,2-diisobutyl-1,3-dimethoxypropane, and 1.17 ml  $\text{TiCl}_4$ . The jar was placed in a centrifugal mill operated at 350 rpm for 20 hours.

In a 350 ml glass reactor, equipped with porous disk for filtration, condenser, mechanical agitator and thermometer, was introduced at room temperature under an anhydrous nitrogen environment, 8 g of the above milled product and 32 ml 1,2-dichloroethane. The contents were heated at 83°C for 2 hours, then filtered and the solid residue washed 3 times with 50 ml portions of anhydrous hexane. The solid residue obtained by vacuum drying contained 1.5% Ti and 18.4% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure B.2 using 0.57 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  and 0.5 ml hexane suspension containing 81 mg solid catalyst component.

188 g of polymer was obtained with polymer yield of 2.3 Kg/g catalyst component, a 94.7% residue insoluble in xylene, at 25°C a melt index of 8.4 g/10', and tamped bulk density of 0.29 g/ml.

#### Example 5

In a 500 ml glass flask equipped with a condenser, mechanical agitator and thermometer, was introduced, at room temperature under anhydrous nitrogen atmosphere, 250 ml of  $\text{TiCl}_4$  and 25 g of support in spherical particles comprising a styrene-divinylbenzene copolymer impregnated with the  $\text{MgCl}_2 \cdot 2\text{Ti}(\text{OC}_4\text{H}_9)_4$  complex, prepared according to procedure of example 1 of U.S. patent application SN 07/359,234.

While agitating, the contents were heated to 100°C. When the temperature reaches 40°C, 1.52 ml of 2,2-diisobutyl-1,3-dimethoxypropane was introduced. The temperature maintained at 100°C for 1 hour, the solid allowed to settle and the supernatant was removed by siphon. An additional 250 ml  $\text{TiCl}_4$  was fed and heated at 120°C for 2 hours. After settlement of the solids and siphoning of the supernatant, the solid residue was washed 5 times with 150 ml portions of anhydrous heptane at 85°C, then 3 times with anhydrous hexane at room temperature, until no chlorine ions were formed in the wash liquid.

After vacuum drying, the solid catalytic component contained 0.77% Ti and 3.9% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure A.1 using 0.79 g  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 1.4 ml hexane suspension containing 49.5 mg solid catalyst component and 1300 ml hydrogen. 400 g of polymer was obtained with a polymer yield of 8.1 kg/g catalyst component, a 95.1% insoluble residue in xylene, at 25°C, a melt index of 11.2 g/10' and a tamped bulk density of 0.42 g/ml.

#### Example 6

In a 500 ml glass flask equipped with condenser, mechanical agitator and thermometer was introduced 156.9 ml  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  and 20 g anhydrous  $\text{MgCl}_2$ . While agitating, the contents were heated to 140°C for 3 hours, cooled to 40°C and the resulting solution diluted with 157 ml anhydrous heptane. Then 31.5 ml polymethylhydroxyloxane was added ( $d=0.99 \text{ g/ml}$ ,  $M_w=2256$ ). After allowing the solvents to settle and siphoning off the supernatant, the solid was washed 3 times with 150 ml portions of anhydrous heptane.

At 50°C, 18.4 ml of  $\text{SiCl}_4$  was added over a 15 minutes period, then treated with 2.7 ml 2,2-diisobutyl-1,3-dimethoxypropane and maintained at 50°C for 2 hours. The solids were allowed to settle and the supernatant removed by siphon and washed 4 times with 120 ml portions of anhydrous hexane. The residue was treated with 52.3 ml of  $\text{TiCl}_4$  and then heated at 90°C for 2 hours. The liquid was removed by siphon after the solids were allowed to settle, the solid residue was washed repeatedly with anhydrous heptane at 60°C and then 5 times at room temperature, until there were no chlorine ions in the wash liquid. After vacuum drying, the solid catalyst component contained 1.65% Ti and 14.9% 2,2-diisobutyl-1,3-dimethoxypropane.

Propylene was polymerized according to procedure B.2 using 0.57 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  and 0.4 ml hexane suspension containing 7.9 mg solid catalyst component. 229 g of polymer was obtained with a polymer yield of 29 kg per g; of catalyst component 96.2% insoluble residue in xylene at 25°C and a tamped bulk density 10 AD of 0.42 g/cc.

55

#### Example 7

Into a 1 l glass flask equipped with condenser, mechanical agitator and thermometer, under anhydrous nitrogen atmosphere, was introduced 572 ml solution containing 11.4 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  for each 100 ml hexane.

While agitating at 5°C, 40 g spherical  $MgCl_2 \cdot 2.6C_2H_5OH$  support, prepared according to method of example 1 in U.S. patent No. 4,469,648 was added over 90 minutes, then heated to 60°C for 3.5 hours, the solids were allowed to settle and the supernatant removed by siphon. The solid residue was washed 10 times with 200 ml portions of anhydrous heptane.

5 To the product obtained, which was diluted to 100 ml with anhydrous heptane, was added over 2 hours at 80°C, 2.7 ml  $n-C_4H_9OH$  diluted with 1.5 ml anhydrous heptane.

The solid were allowed to settle and the liquid siphoned off. The solid was washed repeatedly with 150 ml portions anhydrous hexane. After vacuum drying the solid showed a Mg content of 20.9% and  $C_2H_5OH$  of 3.6%.

10 In a 500 ml glass flask was introduced, under an anhydrous nitrogen environment, 362 ml  $TiCl_4$ , then while agitating at 0°C, 14.5 g of the solid catalyst component obtained above were added. Over a 1 hour period the contents were heated to 100°C. When the temperature reached 40°C, 4.8 ml 2,2-diisobutyl-1,3-dimethoxypropane was added. The contents were heated at 100°C for 2 hours. The solids allowed to settle and the liquid was siphoned off

15 To the solid residue 319 ml of  $TiCl_4$  was added, heated to 120°C for 1 hour, and then the liquid was removed by siphoning after settling. The solid was washed repeatedly with 150 ml portions anhydrous hexane first at 60°C and then at room temperature. After vacuum drying the catalytic solid contains 2.45% Ti and 6.3% 2,2-diisobutyl-1,3-dimethoxypropane.

20 Propylene was polymerized according to procedure A.1 using 0.76 g  $Al(C_2H_5)_3$ , 0.09 ml hexane solution containing 8.9 mg solid catalyst component and 1000 ml hydrogen. 430 g of polymer was obtained with a polymer yield of 51.8 Kg/g catalyst component, 90.4% insoluble residue in xylene at 25°C, a melt index of 8.9 g/10' and a tamped bulk density of 0.49 g/ml.

Examples 8-18 and comparative examples 1-3

25 Into a 500 ml reactor equipped with filtering disk 225 ml  $TiCl_4$  was introduced at 0°C. While agitating 10.1 g (54 mmoles) microspheroidal  $MgCl_2 \cdot 2C_2H_5OH$ , obtained according to the method of example 1 of U.S. patent 4,469,648, was added. Upon completing the addition, the temperature was brought to 40°C and 9 mmoles ether was introduced. The temperature was raised to 100°C over one hour period and allowed to react for 2 hours after which the unreacted  $TiCl_4$  was removed by filtration. Another 200 ml  $TiCl_4$  was added and allowed to react at 120°C for 1 hour, filtered and washed with  $n$ -heptane at 60°C until the chlorine ions disappeared from the filtrate.

30 The ethers used and the analytical data relative to the solid catalyst component obtained in this manner are reported in table 2.

35

40

45

50

55

Examples 19-36 and comparative examples 4-6

The polymerization data with the catalysts obtained from the solid catalyst components prepared according to examples 8-18 and comparative examples 1-3 are reported in table 3.

Table 2

Ex. No.	Ether used	Composition of the solid catalyst		
		Mg	Ti	Ether
<hr/>				
8	2,2-dimethyl- 1,3-dimethoxypropane	2.6		10.40
9	2-isopropyl-2-methyl- 1,3-dimethoxypropane	21.7	3.24	10.44
10	2,2-diisobutyl- 1,3-dimethoxypropane	16.64	3.1	15.5
11	2,2-diisobutyl- 1,3-diethoxypropane		4.3	8.10
12	2,2-diisobutyl- 1,3-di-n-butoxypropane	16.3	5.2	2.40
13	2,2-diphenyl- 1,3-dimethoxypropane	14.5	5.59	11.10
14	2,2-bis (cyclohexylmethyl) 1,3-dimethoxypropane	14.87	4.43	11.4
15	1,3-diisobutoxypropane		4.7	0.005
16	2,2-pentamethylene 1,3-dimethoxypropane		2.9	15.1
17	1,1-bis (methoxymethyl) bicyclo- (2,2,1)-heptane		3.3	11.7
18	2-isopentyl-2-isopropyl- 1,3-dimethoxypropane		2.5	14.8

Table 2 (follow)

5

10	Comp. 1	1,3 dimethoxypropane	18.0	1.7	10.6
15	Comp. 2	1-isopropyl-2,2-dimethyl 1,3-dimethoxypropane	17.0	4.3	0
20	Comp. 3	1,2-dimethoxyethane	20.8	3.0	4.0

25

30

35

40

45

50

55

Table 3

5	Ex.	Catalyst Com- ponent	Polymer Yield	I.I.	Polymerization	
	No.	Ex.No.	g polymer/gCat. comp.	%	dl/g	Method
<hr/>						
10	19	8	3100	89.8	2.15	B.2.1.
	20	9	8700	93.3	2.90	B.2.1.
15	21	10	9300	95.3		B.2.1.
	22	11	14200	79.7		B.2.1.
	23	12	13600	84.3	2.10	B.2.1.
20	24	13	9100	84.8	2.48	B.2.1.
	25	14	19000	88.4	1.65	B.2.1.
	26	15	20100	75.0		B.2.1.
25	27	16	7100	89.3		B.2.1.
	28	17	8500	79.8		B.2.1.
	29	18	11000	98.0		B.2.1.
30	Comp. 4	Comp. 1	1800	64.9		B.2.1.
<hr/>						
35	Comp. 5	Comp. 2	2000	72.0	1.0	B.2.1.
	Comp. 6	Comp. 3	4300	68.1	1.77	B.2.1.
40	30	10 (dimethyl dimethoxysilane)	8900	96.1	2.39	B.2.2.
45	31	10 (2,2-diisobutyl-1,3-dimethoxypropane)	7900	96.3	2.00	B.2.2.

Table 3 (follow)

5

10	32	10	5100	97.5	2.15	B . 2 . 2 .
(phenyltriethoxysilane)						
15	33	10	33400	92.0	1.56	A.1.
(2,2-diisobutyl-1,3-dimethoxypropane)						
20	34	10	23200	96.0	1.71	A.1.1.
(2,2,6,6-tetramethylpiperidine)						
25	35	10	36600	93.8	1.83	A.1.1.
(ethyl p.toluate)						
30	<hr/>					

25

Example 37

30 A 1.4 stainless steel autoclave, equipped with a thermostat and mechanical agitator, was purged with gaseous propylene at room temperature for 1 hour. Then, while agitating, 66 g of butadiene, 230 g of liquid propylene and 300 ml of hydrogen were fed. Under propylene pressure a catalytic suspension of 0.6 Al(Et<sub>3</sub>)<sub>3</sub> TEAL and 0.048 g solid catalyst component of example 1. The temperature was rapidly brought to 70°C (in 5 min) and the resulting pressure was 24.6 atm. These conditions were maintained for 4 hours reintegrating feeding propylene continuously to reintegrate the portion polymerized. The autoclave was then degassed and cooled at room temperature. 64 g polymer, dried in an oven under nitrogen at 60°C for 4 hours, was recovered, with a yield of 1333 g polymer per g catalyst. When analyzed, using standard methods, the polymer showed the following characteristics:

35 [η] in tetrahydronaphthalene at 135°C = 1.8 dl/g.

MIL = 4 g/10'

Soluble in xylene at 25°C = 24.1% (weight).

Butadiene content (determined via IR):

40 - raw polymer = 0.6% 1,2; 3.7% 1,4 trans

- insoluble in xylene = 0.5% 1,2; 1.6% 1,4 trans

- soluble in xylene = < 0.25% 1,2; 8.2 1,4 trans.

Example 38

50

The autoclave and procedure of example 37 was used to polymerize propylene with the solid catalyst component of example 1, but using instead of Al-triethyl, a mixture of 3.3 mmoles Al-triethyl and 3.3 mmoles Al-diethylmonochloride and 0.018 g solid catalyst component.

380 g of a polymer with a polymer yield of 35.2 kg/g of catalyst component, a 94.1% insoluble residue in xylene at 25°C, and a melt index of 7.3 g/10'.

Example 39

In the same autoclave used in example 1 was charged at 30°C and without agitation, a catalyst suspension of 0.9 g Al-triethyl and 0.09 g of the solid catalyst component of example 37 in about 18 ml hexane. Then 800 g propane was introduced with agitation. The temperature was rapidly brought to 75°C, and then 2 atm hydrogen, 200 g butene-1 were introduced. Ethylene was then introduced until the pressure reached 33 atm. These conditions were maintained for 2 hours maintaining constant pressure by continuously feeding with a mixture of ethylene and butene-1 in a weight ratio of 10/1.

The autoclave was degassed and cooled at room temperature.

The amount of polymer, obtained after drying at 70°C under nitrogen for 4 hours, was 280 g, which corresponded to a yield of 31.1 kg per g of catalyst component.

Analyzed using standard methods, the product showed the following characteristics:

- MIE = 0.23 g/10' (F/E = 26.7)
- MIF = 6.16 g/10'
- Butene (determined via IR) = 6% (weight)
- Density = 0.9211 g/cm<sup>3</sup>
- Soluble in xylene at 25°C = 6.3% (weight)

Example 40

In the same autoclave used in example 3 purged as described therein but using ethylene instead of propylene, was introduced at 45°C under hydrogen flow, a 900 ml solution of 0.5 g/l of Al-triisobutyl in anhydrous hexane and immediately after 0.015 g of solid catalyst component of example 1 suspended in 100 ml of the above mentioned solution. The contents were rapidly heated to a temperature of 75°C, then hydrogen was fed until the pressure reached 4.5 atm. These conditions were maintained for 3 hours continuously replacing the ethylene polymerized. The autoclave was rapidly degassed and cooled at room temperature. The polymeric suspension was filtered and the solid was dried at 60°C under nitrogen for 8 hours.

300 g of polymer was obtained (corresponding to a yield of 20 kg/g of catalyst component) which had the following characteristics (determined by standard methods):

- MIE = 1.74 g/10' (MIF/MIE = 26.5)
- MIF = 46 g/10'
- $[\eta]$  135°C THN = 1.78 dl/g
- tamped bulk density = 0.362 g/ml

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

Examples 41-51

Catalyst components are prepared according to the procedure of examples 8-18 by using different ethers. The ethers used and the analytical data relative to the solid catalyst component obtained in this matter are reported in Table 4.

Examples 52-62

The polymerization data with the catalyst obtained from the solid catalyst components prepared according to examples 41-51 are reported in Table 5.

5

Table 4

Ex. No.	Ether used	Composition of the solid catalyst		
		Mg	Ti	Ether
41	2-isopropyl-2- 3,7 dimethyloctyl-1,3- dimethoxypropane	13.4	3.3	17.6
42	2,2-diisopropyl-1,3- dimethoxypropane	16.1	3.2	13.8
43	2-isopropyl-2- cyclohexylmethyl-1,3- dimethoxypropane	14.3	3.7	14.5
44	2,2-dicyclohexyl-1,3- dimethoxypropane	16.0	4.5	15.3
45	2-isopropyl-2-isobutyl-1,3- dimethoxypropane	16.0	3.6	14.5
46	2,2-diisopentyl-1,3- dimethoxypropane	15.1	3.1	11.3
47	2,2-dipropyl-1,3- dimethoxypropane	14.3	2.1	18.3
48	2-isopropyl-2-cyclohexyl- 1,3-dimethoxypropane	16.1	3.2	14.8
49	2-isopropyl-2-cyclopentyl- 1,3-dimethoxypropane	15.0	2.6	13.4
50	2,2-dicyclopentyl-1,3- dimethoxypropane	15.5	3.4	16.2
51	2-heptyl-2-pentyl-1,3- dimethoxypropane	14.4	4.6	16.0

Table 5

5	Ex.	Catalyst	Polymer yield	I.I	{M} dl/g	Polymerization
	No.	Ex.No.	g polymer/gCat. comp.	%		Method
10	52	41	12190	91.5	1.85	B.2.1.
	53	42	10750	95.9	1.88	B.2.1.
	54	43	8410	94.2	1.76	B.2.1.
15	55	44	22900	95.7	2.27	B.2.1.
	56	45	16000	95.5	2.32	B.2.1.
	57	46	18900	96	1.48	B.2.1.
20	58	47	13000	94.6	1.74	B.2.1.
	59	48	22200	95	1.72	B.2.1.
	60	49	19000	96.2	1.66	B.2.1.
25	61	50	12000	95.5	1.90	B.2.1.
	62	51	20600	88	1.72	B.2.1

30

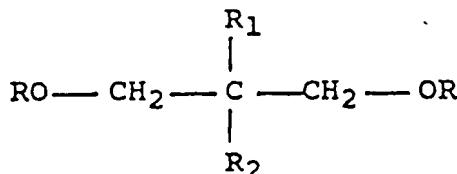
## Claims

1. A solid catalyst component for the polymerization of olefins comprising a magnesium dihalide in active form and supported thereon a titanium compound containing at least one Ti-halogen bond and an electron-donor compound selected from ethers containing two or more ether groups, said ethers being capable of forming complexes with activated anhydrous magnesium dichloride at less than 60 mmoles per 100 g of activated anhydrous magnesium dichloride and of entering into substitution reactions with  $TiCl_4$  at less than 50 % by moles; the ether complexing test with  $MgCl_2$  being conducted as follows:  
in a 100 ml glass flask with fixed blades glass mechanical agitator are introduced in a nitrogen atmosphere, in order:
  - 70 ml anhydrous n-heptane
  - 12 mmoles activated anhydrous  $MgCl_2$
  - 2 mmoles ether;
- 45 the ingredients are heated at 60°C for 4 hours (stirring speed 400 rpm), then filtered and washed at room temperature with 100 ml n-heptane and dried with mechanical pump;  
the quantity of ether complexed is determined, after treatment of the solid with 100 ml of ethanol by quantitative gaschromatographic analysis;
- 50 and the test for reactivity of the ethers with  $TiCl_4$  being conducted as follows:  
in a 25 ml test tube with a magnetic agitator are introduced, in a nitrogen atmosphere, in order:
  - 10 ml anhydrous n-heptane
  - 5 mmoles  $TiCl_4$
  - 1 mmole ether donor;

55 the ingredients are heated at 70°C for 30 min, then cooled at 25°C and decomposed with 90 ml of ethanol;  
the solution obtained is analyzed gas chromatographically with a Carlo Erba HRGC 5300 Mega Series gas chromatograph with a 25 meters Chrompack CP-SIL 5 CB capillary column.

2. The solid catalyst component of claim 1 where the ethers are characterized by the formation of complexes with activated anhydrous magnesium dichloride in quantities between 20 and 50 mmoles per 100 g of activated magnesium dichloride.

5 3. The solid catalyst component of claim 1 wherein the ethers are selected from diethers having the following general formula:



15 where  $\text{R}$ ,  $\text{R}_1$  and  $\text{R}_2$ , independently, are linear or branched alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms and  $\text{R}_1$  or  $\text{R}_2$  may also be hydrogen.

20 4. The solid catalyst component of claim 3 wherein  $\text{R}$  is methyl, and when  $\text{R}_1$  is methyl, ethyl, propyl or isopropyl,  $\text{R}_2$  is ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, 2-ethylhexyl, cyclohexyl, methylcyclohexyl, phenyl or benzyl, and when  $\text{R}_1$  and  $\text{R}_2$  are the same, they are ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, neopentyl, isopentyl, phenyl, benzyl, cyclopentyl or cyclohexyl.

25 5. The solid catalyst component of claim 3 wherein  $\text{R}$  is methyl and  $\text{R}_1$  and  $\text{R}_2$  are different and are isopropyl, isobutyl, t-butyl, cyclohexyl, isopentyl or cyclohexylethyl.

30 6. The solid catalyst component of claim 3 where the ethers are 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane, 2,2-bis(cyclohexyl-methyl)-1,3-dimethoxypropane, 2-isopropyl-2,3,7-dimethylocetyl-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-isobutyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane.

35 7. The solid catalyst component of one or more of the preceding claims wherein the titanium compound is selected from the group consisting of the halo alcoholates and the halides of titanium and the magnesium dihalide is magnesium dichloride.

40 8. The solid catalytic component of claim 7 wherein the titanium compound is titanium tetrachloride.

45 9. The solid catalytic component of claim 7 wherein the magnesium dichloride is present in active form characterized in that in the X-ray powder spectrum of the catalyst component a halo appears instead of the most intense diffraction line which appears at an interplanar distance of 2.56 Å in the non-activated magnesium dichloride and the maximum intensity of the halo is shifted with respect to said interplanar distance.

50 10. The solid catalyst component of one or more of the preceding claims wherein the ether is present in an amount between 5 and 20% mmoles with respect to the magnesium dihalide.

11. The solid catalyst component of one or more of the preceding claims wherein the Mg/Ti ratio is between 30:1 and 4:1.

12. The solid catalyst component of one or more of the preceding claims wherein the magnesium dichloride in active form is obtained from  $\text{MgCl}_2$  complexes with alcohols or titanium alcoholates, or from alcoholates and chloroalcoholates of magnesium.

55 13. The solid catalyst component of one or more of the preceding claims wherein the magnesium dichloride and the titanium compound are supported on resins and the Mg/Ti ratio is from 2:1 to 3:1.

14. A catalyst for the polymerization of olefins  $\text{CH}_2=\text{CHR}$ , wherein R is H, an alkyl radical with 1-6 carbon atoms or an aryl, or mixtures thereof with or without a diolefin, comprising the product obtained by reaction of a solid catalyst component of claim 3 with an Al-alkyl compound.

5 15. The catalyst of claim 14 wherein the Al-alkyl compound is an Al-trialkyl.

16. The catalyst of claim 15 for the polymerization of olefins  $\text{CH}_2=\text{CHR}$  wherein R is an alkyl radical with 1-6 carbon atoms, further comprising, in addition to the Al-trialkyl compound 2,2,6,6-tetramethylpiperidine or a silicon electron donor compound containing at least one Si-OR bond wherein R is a hydrocarbon radical.

10 **Patentansprüche**

15 1. Feste Katalysatorkomponente zur Polymerisation von Olefinen, umfassend ein Magnesiumdihalogenid in aktiver Form und hierauf aufgebracht eine Titanverbindung, die zumindest eine Ti-Halogenbindung enthält, und eine Elektronen-Donor-Verbindung, ausgewählt unter Ethern, die zwei oder mehrere Ethergruppen enthalten, wobei die Ether zur Bildung von Komplexen mit aktiviertem, wasserfreiem Magnesiumdichlorid bei weniger als 60 mMol/100 g aktiviertes, wasserfreies Magnesiumdichlorid und zu einer Teilnahme an Substitutionsreaktionen mit  $\text{TiCl}_4$  zu weniger als 50 Mol-% befähigt sind;

20 wobei der Ether-Komplexbildungstest mit  $\text{MgCl}_2$  wie folgt durchgeführt wird:  
in einen 100 ml Glaskolben mit fixiertem, mechanischem Glasblatt-Rührer bringt man unter einer Stickstoffatmosphäre der Reihenfolge nach ein:

- 70 ml wasserfreies n-Heptan
- 12 mMol aktiviertes, wasserfreies  $\text{MgCl}_2$
- 2 mMol Ether;

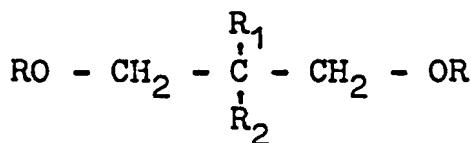
25 die Bestandteile werden 4 Stunden bei 60°C (Rührgeschwindigkeit 400 U/min) erhitzt, hiernach filtriert und bei Raumtemperatur mit 100 ml n-Heptan gewaschen und mit einer mechanischen Pumpe getrocknet;  
30 die Menge an komplexiertem Ether wird nach Behandeln des Feststoffs mit 100 ml Ethanol durch quantitative gas-chromatographische Analyse bestimmt;  
und wobei der Test für die Reaktivität der Ether mit  $\text{TiCl}_4$  wie folgt durchgeführt wird:  
In ein 25 ml Testrohr mit Magnetrührer bringt man unter einer Stickstoffatmosphäre der Reihenfolge nach ein:

- 10 ml wasserfreies n-Heptan
- 5 mMol  $\text{TiCl}_4$
- 1 mMol Ether-Donor;

35 die Bestandteile werden 30 Minuten bei 70°C erhitzt, hiernach bei 25°C abgekühlt und mit 90 ml Ethanol zersetzt;  
40 die erhaltene Lösung wird gaschromatographisch mit einem Carlo Erba HRGC 5300 Mega Series-Gaschromatographen mit einer 25 Meter Chrompack CP-SIL 5 CB-Kapillarsäule analysiert.

45 2. Feste Katalysatorkomponente gemäß Anspruch 1, worin die Ether durch die Bildung von Komplexen mit aktiviertem, wasserfreiem Magnesiumdichlorid in Mengen zwischen 20 und 50 mMol/100 g aktiviertes Magnesiumdichlorid gekennzeichnet sind.

50 3. Feste Katalysatorkomponente gemäß Anspruch 1, worin die Ether unter Diethers der folgenden allgemeinen Formel



55 worin R, R<sub>1</sub> und R<sub>2</sub> unabhängig lineare oder verzweigte Alkyl-, cycloaliphatische, Aryl-, Alkaryl- oder Aralkylreste mit 1 bis 18 Kohlenstoffatomen sind und R<sub>1</sub> und R<sub>2</sub> auch Wasserstoff bedeuten können.

4. Feste Katalysatorkomponente gemäß Anspruch 3, worin R Methyl ist, und wenn R<sub>1</sub> Methyl, Ethyl, Propyl oder Isopropyl ist, R<sub>2</sub> Ethyl, Propyl, Isopropyl, Butyl, Isobutyl, tert.-Butyl, 2-Ethylhexyl, Cyclohexyl, Methylcyclohexyl, Phenyl

oder Benzyl bedeutet, und wenn R<sub>1</sub> und R<sub>2</sub> gleich sind, diese Ethyl, Propyl, Isopropyl, Butyl, Isobutyl, tert.-Butyl, Neopentyl, Isopentyl, Phenyl, Benzyl, Cyclopentyl oder Cyclohexyl sind.

5. Feste Katalysatorkomponente gemäß Anspruch 3, worin R für Methyl steht und R<sub>1</sub> und R<sub>2</sub> verschieden sind und  
Isopropyl, Isobutyl, tert.-Butyl, Cyclohexyl, Isopentyl oder Cyclohexylethyl bedeuten.

6. Feste Katalysatorkomponente gemäß Anspruch 3, worin die Ether 2,2-Diisobutyl-1,3-dimethoxypropan, 2-Isopropyl-  
2-isopentyl-1,3-dimethoxypropan, 2,2-Bis-(cyclohexyl-methyl)-1,3-dimethoxypropan, 2-Isopropyl-2,3,7-dimethyloc-  
tyl-1,3-dimethoxypropan, 2,2-Diisopropyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclohexylmethyl-1,3-dimethoxypro-  
pan, 2,2-Dicyclohexyl-1,3-dimethoxypropan, 2-Isopropyl-2-isobutyl-1,3-dimethoxypropan, 2,2-Diisopentyl-1,3-  
dimethoxypropan, 2,2-Dipropyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclohexyl-1,3-dimethoxypropan, 2-Isopropyl-  
2-cyclopentyl-1,3-dimethoxypropan, 2,2-Dicyclopentyl-1,3-dimethoxypropan, 2-Heptyl-2-pentyl-1,3-dimethoxypro-  
pan sind.

15. 7. Feste Katalysatorkomponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin die Titanver-  
bindung unter Haloalkoholaten und Halogeniden von Titan ausgewählt ist und das Magnesiumdihalogenid Magne-  
siumdichlorid ist.

20. 8. Feste Katalysatorkomponente gemäß Anspruch 7, worin die Titanverbindung Titantrachlorid ist.

25. 9. Feste Katalysatorkomponente gemäß Anspruch 7, worin das Magnesiumdichlorid in aktiver Form vorliegt, gekenn-  
zeichnet dadurch, daß in dem Röntgenbeugungspulverspektrum der Katalysatorkomponente ein Halo erscheint  
anstelle der intensivsten Beugungslinie, die bei einem interplanaren Abstand von 2,56 Å in dem nichtaktivierten  
Magnesiumdichlorid erscheint, und die maximale Intensität des Halos im Hinblick auf diesen interplanaren Abstand  
verschoben ist.

30. 10. Feste Katalysatorkomponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin der Ether in  
einer Menge zwischen 5 und 20 Mol-%, bezogen auf das Magnesiumdihalogenid, vorliegt.

35. 11. Feste Katalysatorkomponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin das Mg/Ti-Ver-  
hältnis zwischen 30:1 und 4:1 beträgt.

40. 12. Feste Katalysatorkomponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin das Magnesi-  
umdichlorid in aktiver Form aus MgCl<sub>2</sub>-Komplexen mit Alkoholen oder Titanalkoholaten oder aus Alkoholaten und  
Chloralkoholaten von Magnesium erhalten wird.

45. 13. Feste Katalysatorkomponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin das Magnesi-  
umdichlorid und die Titanverbindung auf Harzen aufgebracht sind und das Mg/Ti-Verhältnis von 2:1 bis 3:1 beträgt.

50. 14. Katalysator für die Polymerisation von Olefinen CH<sub>2</sub>=CHR, worin R für H, einen Alkylrest mit 1 bis 6 Kohlenstoff-  
atomen oder ein Aryl steht, oder von Mischungen hiervon mit oder ohne ein Diolefin, umfassend das Produkt, erhalten  
durch Reaktion einer festen Katalysatorkomponente gemäß Anspruch 3 mit einer Al-alkylverbindung.

15. Katalysator gemäß Anspruch 14, worin die Al-alkylverbindung ein Al-trialkyl ist.

45. 16. Katalysator gemäß Anspruch 15 zur Polymerisation von Olefinen CH<sub>2</sub>=CHR, worin R für einen Alkylrest mit 1 bis  
6 Kohlenstoffatomen steht, weiterhin umfassend, zusätzlich zu der Al-trialkylverbindung, 2,2,6,6-Tetramethylpiperi-  
din oder eine Silicium-Elektronen-Donor-Verbindung mit zumindest einer Si-OR-Bindung, worin R für einen Koh-  
lenwasserstoffrest steht.

## Revendications

1. Constituant solide de catalyseur pour la polymérisation d'oléfines comprenant un dihalogénure de magnésium sous  
forme active et, supporté sur celui-ci, un dérivé de titane contenant au moins une liaison Ti-halogène et un dérivé  
électrodonneur choisi parmi les éthers contenant deux ou plusieurs groupes éther, lesdits éthers étant capables de  
former des complexes avec le dichlorure de magnésium anhydre activé à moins de 60 mmoles par 100 g de dichlo-  
rure de magnésium anhydre activé et d'entrer dans des réactions de substitution avec TiCl<sub>4</sub> à moins de 50% en  
moles;

l'essai de complexation de l'éther avec MgCl<sub>2</sub> étant effectué par la méthode suivante:

dans un ballon en verre de 100 ml équipé d'un agitateur mécanique en verre à lames fixes, on introduit, sous atmosphère d'azote, dans l'ordre:

- 70 ml de n-heptane anhydre,
- 12 mmoles de  $MgCl_2$  anhydre activé,
- 2 mmoles d'éther;

on chauffe le mélange à 60°C pendant 4 heures (sous agitation à 400 tours par minute), puis on filtre et on lave à la température ambiante à l'aide de 100 ml de n-heptane et on sèche à l'aide d'une pompe mécanique;

on détermine la quantité d'éther complexé, après traitement du solide par 100 ml d'éthanol, par analyse chromatographique en phase gazeuse quantitative;

et on effectue le test de réactivité des éthers avec  $TiCl_4$  de la manière suivante:

dans un tube à essai de 25 ml équipé d'un agitateur magnétique, on introduit, sous atmosphère d'azote, dans l'ordre:

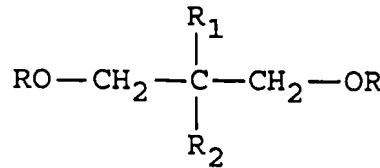
- 10 ml de n-heptane anhydre,
- 5 mmoles de  $TiCl_4$ ,
- 1 mmole d'éther donneur;

on chauffe le mélange à 70°C pendant 30 minutes, puis on refroidit à 25°C et on décompose par 90 ml d'éthanol;

on analyse la solution obtenue par chromatographie en phase gazeuse en utilisant un chromatographe en phase gazeuse Carlo Erba HRGC 5300 Mega Series comportant une colonne capillaire Chrompack CP-SIL 5 CB de 25 mètres.

2. Le constituant solide de catalyseur selon la revendication 1, dans lequel les éthers sont caractérisés par la formation de complexes avec le dichlorure de magnésium anhydre activé en des quantités de 20 à 50 mmoles par 100 g de chlorure de magnésium activé.

3. Le constituant solide de catalyseur selon la revendication 1, dans lequel les éthers sont choisis parmi les diéthers répondant à la formule générale suivante:



dans laquelle:

40 R,  $R_1$  et  $R_2$ , indépendamment les uns des autres, sont des radicaux alkyle linéaires ou ramifiés, cycloaliphatiques, aryle, alkylaryl ou arylalkyle comportant 1 à 18 atomes de carbone; et

45  $R_1$  ou  $R_2$  peut également être un atome d'hydrogène.

4. Le constituant solide de catalyseur selon la revendication 3, dans lequel R est un radical méthyle et si  $R_1$  est un radical méthyle, éthyle, propyle ou isopropyle,  $R_2$  est un radical éthyle, propyle, isopropyle, butyle, isobutyle, t-butyle, 2-éthylhexyle, cyclohexyle, méthylcyclohexyle, phényle ou benzyle; et si  $R_1$  et  $R_2$  sont identiques, ils sont des radicaux éthyle, propyle, isopropyle, butyle, isobutyle, t-butyle, néopentyle, isopentyle, phényle, benzyle, cyclopentyle ou cyclohexyle.

5. Le constituant solide de catalyseur selon la revendication 3, dans lequel R est un radical méthyle et  $R_1$  et  $R_2$  sont différents et sont des radicaux isopropyle, isobutyle, t-butyle, cyclohexyle, isopentyle ou cyclohexyléthyle.

6. Le constituant solide de catalyseur selon la revendication 3, dans lequel les éthers sont: 2,2-diisobutyl-1,3-diméthoxypropane, 2-isopropyl-2-isopentyl-1,3-diméthoxypropane, 2,2-bis-(cyclohexylméthyl)-1,3-diméthoxypropane, 2-isopropyl-2-3,7-diméthylloctyl-1,3-diméthoxypropane, 2,2-diisopropyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclohexylméthyl-1,3-diméthoxypropane, 2,2-dicyclohexyl-1,3-diméthoxypropane, 2-isopropyl-2-isobutyl-1,3-diméthoxypropane, 2,2-diisopentyl-1,3-diméthoxypropane, 2,2-dipropyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclo-

hexyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclopentyl-1,3-diméthoxypropane, 2,2-dicyclopentyl-1,3-diméthoxypropane, 2-heptyl-2-pentyl-1,3-diméthoxypropane.

7. Le constituant solide de catalyseur selon une ou plusieurs des revendications 1 à 6, dans lequel le dérivé de titane est choisi dans le groupe consistant en les haloalcoolates et les halogénures de titane et le dihalogénure de magnésium est le dichlorure de magnésium.

10 8. Le constituant solide de catalyseur selon la revendication 7, dans lequel le dérivé de titane est le tétrachlorure de titane.

15 9. Le constituant solide de catalyseur selon la revendication 7, dans lequel le dichlorure de magnésium est présent sous une forme active, caractérisé en ce que le spectre de poudre aux rayons X du constituant de catalyseur présente un halo à la place de la raie de diffraction la plus intense qui apparaît à une distance interplanaire de 2,56 Angstroems dans le dichlorure de magnésium non active, et l'intensité maximum du halo est décalée par rapport à ladite distance interplanaire.

20 10. Le constituant solide de catalyseur selon une ou plusieurs des revendications 1 à 9, dans lequel l'éther est présent en une quantité comprise entre 5 et 20% en mmoles par rapport au dihalogénure de magnésium.

25 11. Le constituant solide de catalyseur selon une ou plusieurs des revendications 1 à 10, dans lequel le rapport Mg/Ti est compris entre 30/1 à 4/1.

12. Le constituant solide de catalyseur selon une ou plusieurs des revendications 1 à 11, dans lequel le dichlorure de magnésium sous forme active s'obtient à partir de complexes de  $MgCl_2$  avec des alcools ou des alcoolates de titane ou à partir d'alcoolates ou de chloroalcoolates de magnésium.

30 13. Le constituant solide de catalyseur selon une ou plusieurs des revendications 1 à 12, dans lequel le dichlorure de magnésium et le dérivé de titane sont supportés sur des résines et le rapport Mg/Ti est de 2/1 à 3/1.

14. Un catalyseur pour la polymérisation d'oléfines  $CH_2=CHR$ , où R est un atome d'hydrogène, un radical alkyle comportant 1 à 6 atomes de carbone ou un radical aryle, ou leurs mélanges, avec ou sans une dioléfine, comprenant le produit obtenu par la réaction d'un constituant solide de catalyseur selon la revendication 3, avec un dérivé alkyl-Al.

35 15. Le catalyseur selon la revendication 14, dans lequel le dérivé alkyl-Al est un trialkyl-Al.

16. Le catalyseur selon la revendication 15, pour la polymérisation des oléfines  $CH_2=CHR$ , où R est un radical alkyle comportant 1 à 6 atomes de carbone, comprenant, en outre, en plus du dérivé trialkyl-Al, de la 2,2,6,6-tétraméthyl-pipéridine ou un dérivé électrodonneur du silicium contenant au moins une liaison Si-OR où R est un radical hydrocarboné.

40

45

50

55